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These two volumes are an essential requirement for anyone with a desire to learn about material interface with corrosive environments, including students of the subject, designers, materials engineers, mechanical engineers and many others.

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18.7 Rubber and Synthetic Elastomers

In 1839 Charles Goodyear discovered that raw rubber when mixed with finely divided sulphur and heated to 150°C, changed from a soft deformable substance into a tough resilient material. This reaction was called vulcanisation. Rubber linings have been in use for some 130 years for the protection of substances against chemical attack. In 1855, J. H. Johnson took out a patent for spinning components made from metal covered with rubber, thus combining the strength and durability of the metal with the non liability to oxidation of the rubber. In 1857, Thomas Hancock published his *Personal Narrative* which included details of the outstanding resistance of natural rubber to chemical compounds. In his summary, Hancock described sheets of a mixture of one part of natural rubber to two parts of pitch for the protection of ships' hulls. He listed moulded articles made from hard vulcanisates which were resistant to acids, alkalis and chemical solutions and also mentions vulcanised sheet rubber for use as linings in chemical vessels.

The excellent chemical resistance of ebonite was recognised at this time, and patents for the use of ebonite as a lining material were applied for in 1874 by Thomson and Watson in Great Britain. In 1885, Lacollonge in France was granted a patent for a lining composed of an underlay of ebonite with soft rubber on the exposed surface. Whilst ebonite linings had proved satisfactory in static applications, they had proved to be unsuitable for transportation work due to brittleness. In 1924, B. F. Goodrich introduced the Vulcalock bonding system, which used a cyclised rubber-based primer, thus enabling soft rubber to be bonded directly to a metal substrate.

Prior to 1940, the use of synthetic elastomers in linings was negligible, but the advent of the Second World War, and the consequent loss of natural rubber sources to the Allies, led to the use of synthetic rubber, namely a styrene-butadiene copolymer which, whilst not having all the properties of natural rubber, proved to have adequate anti-corrosive performance.

The standard polymers used for rubber linings consist of materials that are cross-linkable macromolecules which, on mixing with suitable reactants that form strong chemical bonds, change from a soft deformable substance into an elastic material. These polymers include natural rubber and its corresponding synthetic, *cis*-polyisoprene, styrene-butadiene rubber, polychloroprene, butyl rubber, halogenated butyl rubbers, acrylonitrile-

butadiene rubber, ethylene propylene terpolymer (e.p.d.m.) and chlorosulphonated polyethylene (Hypalon).

With natural rubber and *cis*-polyisoprene the normal cross linking agent used is sulphur. When mixed with natural rubber and heated, the sulphur reacts with the alpha methylenic carbon atoms of adjacent molecules, predominantly by S₁ and S₂ cross links. If a low percentage of sulphur is added, normally about 2% by weight on the rubber, the end product is a soft elastic material.

Ebonites on the other hand contain from 28% to 40% sulphur. When ebonite compounds are vulcanised, the available cross-link sites are saturated and no residual unsaturation remains. In ebonites the sulphur reacts to give two different types of links. About 5% of the sulphur reacts to form cross-links in the normal manner, whilst the remainder forms addition links along the molecular chain. It is the addition links that confer the rigidity to ebonites as the bulky sulphur groups restrict the movement of the molecules when the material is stretched. The greater the percentage of addition links the more rigid, and thus more brittle, the ebonite. Similar reactions are used for cross-linking acrylonitrile butadiene and styrene-butadiene rubbers.

Standard butyl rubber, which is a copolymer of isobutylene with about 2% of isoprene vulcanises in the same manner as natural rubber but, as it only contains a small proportion of polyisoprene, the cross-link percentage is much reduced. It is therefore not possible to make ebonite from a butyl rubber. The same vulcanisation chemistry, with some modifications, applies to ethylene-propylene terpolymers and brominated butyl rubber.

Polychloroprene and Hypalon are usually cross-linked with metal oxides which combine with reactive side groups in the polymer chain.

In general, the reaction mechanism of elastomeric polymers with vulcanisation reagents is slow. Therefore, it is natural to add special accelerators to rubber compounds to speed the reaction. Accelerators are usually organic compounds such as amines, aldehyde-amines, thiazoles, thiurams or dithiocarbamates, either on their own or in various combinations.

Together with the polymer and vulcanisation reagents, rubber lining materials will contain inert fillers such as carbon black, barytes or silicates like china clay. Other ingredients such as plasticisers, tackifiers, stearic acid, zinc oxide and antioxidants are also added to confer the required processing and physical properties on the lining. All the compounding ingredients used must contribute to the maximum chemical resistance of the finished compound coupled with the minimum leach resistance requirements.

Except for standard ebonites and the speciality ambient vulcanising or 'chemical cure' linings, most compounds have the capability of vulcanising both in an autoclave at 150°C or more and in ambient pressure steam or hot water at 100°C. Ebonites are of two types, the autoclave version for factory applications and a highly accelerated version for vulcanising on site at 100°C. Site-lining ebonites with their high acceleration levels are limited with respect to operational temperatures. At temperatures above 70°C, they tend to post vulcanise leading to increased hardness and subsequent brittleness. Leaching of excess, unreacted accelerator can also cause problems, especially in electroplating operations, where contamination may occur with the deposited elemental metal.

Ambient Temperature Vulcanising Lining

A great difficulty, especially on undeveloped sites, is the requirement to raise steam for vulcanising purposes. This problem gives rise to time/cost difficulties, especially with respect to the lining of very large tanks.

In the past 'chemical cure' linings have been employed on a wide scale. These linings, usually based on natural rubber or acrylonitrile-butadiene rubber consist of a standard lining compound with a chemical activator such as dibenzylamine incorporated in the formulation. Prior to the application of the lining to the substrate, the individual sheets of rubber are dipped or brush coated with carbon disulphide or a solution of a xanthogen disulphide in a solvent. The carbon disulphide or xanthogen disulphide permeates the rubber and combines with the dibenzylamine to form an ultra-fast dithiocarbamate accelerator *in situ*, and thus the rubber rapidly vulcanises at ambient temperature.

Such chemical cure methods have been used for many years but, due to the inherent hazards of flammability and toxicity of the system, are not accepted in several countries. Also, if all the exposed working surfaces have not been properly treated, unvulcanised areas may occur which would rapidly deteriorate when the lining is put into service.

In more recent years, lining compounds have been developed that vulcanise at ambient temperatures. Most polymers can be used for such compounds, although most materials are based on natural rubber, acrylonitrile-butadiene rubber and polychloroprene. These compounds contain accelerators which usually give rise to a material which has a delay in the onset of vulcanisation with a subsequent rapid rise in cross-link formation to give full vulcanisation in 6 to 8 weeks. Such materials, unless to be used within a few days of manufacture, are refrigerated to arrest the self-vulcanisation.

The ambient temperature vulcanising of these linings gave rise to exceptional ageing properties both at elevated temperatures and on weathering. This ageing resistance is due to the maximisation of cross-link density at room temperature by avoiding high temperature vulcanisation, with consequent loss of a proportion of the available cross-links.

An alternative to self vulcanising linings is to use prevulcanised rubber sheet linings. The system in modern use is often a butyl rubber from 1·5 to 4·5 mm thick to which is laminated a 1·5 mm thick layer of a polychloroprene compound for adhesion to the substrate. Bonding is carried out with a polychloroprene-based adhesive vulcanised at ambient temperature by the addition of an isocyanate. The system is most often used for lining simple geometry substrates. As it is not possible to ensure that the chemically resistant butyl layer is totally free from pinholes, it is preferable to use such linings in situations where the polychloroprene underlayer will not be attacked by prolonged exposure to the contained environment.

Polyurethane Linings

Whilst some standard elastomers such as natural rubber can be compounded to withstand many abrasive conditions, and to have an acceptable life span,

they are usually limited on severe abrasive duties. In highly abrasive conditions, the use of selected polyurethanes can considerably extend the working life compared with that obtained with standard elastomer linings.

Abrasion-resistant duties may involve abrasion in an aqueous phase or abrasion by dry particulate materials. The selection of the polyurethane type is most important to obtain the best results. Polyester-based polyurethanes perform best in dry abrasion due to their low hysteresis properties and excellent resistance to cut initiation and propagation. However, polyester polyurethanes are susceptible to hydrolytic degradation, and therefore polyether polyurethanes are normally used for aqueous abrasion duties.

Polyester polyurethanes are usually based on a blend of a quasi-prepolymer (polyester/MDI) and a diol/polyester suitable for spray-up operation. An alternative is to use a solvent-containing system using blocked curatives to give an extended pot-life of 2 to 3 hours enabling them to be brush, roller or spray applied.

Polyether polyurethanes are often based on a quasi prepolymer/diol blend reacted with a carbodiimide modified M.D.I. suitable for automatic mix-dispensers.

Excepting polyurethanes which are designed solely for chemical resistance, most abrasion-resistant polyurethanes do not have the chemical resistant capabilities of the other elastomers. Chemical-resistant polyurethanes have elevated temperature limitations, but have proved to have an adequate resistance range especially when contamination by oils and certain solvents have to be handled.

Material Properties

Properties of lining materials are dependent on the formulation and, with polyurethanes, the chemical structure of the final reacted material. The following data on material properties is based on the performance of standard lining compounds. The information given should not be assumed to apply to all linings based on a given elastomer as technological variations may occur from one supplier to another. Thus two linings of equivalent physical properties do not necessarily have the same chemical resistance and working temperature limits.

A summary of the chemical and abrasion resistances, and approximate operational temperature ranges of elastomers is given in Table 18.16. Further details of specific chemical resistances are given in Table 18.17. The maximum temperature of use will always be dependent on the chemical conditions prevailing. Abrasion resistance can be affected by the chemical environment if the exposed surface properties are changed by adsorption or chemical attack. The rate of material loss by abrasion will also vary according to temperature as the resilience etc. is dependent on prevailing temperature conditions.

In general, soft lining compounds made from natural rubber, *cis*-polyisoprene and styrene butadiene rubbers have good chemical resistance to a wide range of inorganic acids, alkalis and their salts and have good abrasion resistance at temperatures up to 100°C. The linings will resist temperatures down to at least -40°C in dynamic working conditions such as empty tank

Lining Sheet Preparation and Application

The rubber sheet is tailored to suit the substrate geometry. The edges of adjacent sheets are normally overlap jointed to avoid steps which could trap air, the joint angle being about 30° face to face. After tailoring, the surface of the sheet to be bonded to the substrate is either swabbed with a solvent or a coat of tack solution is applied. All solvent is then allowed to evaporate prior to applying the sheet to the prepared substrate. The prepared sheet is then positioned on the substrate and rolled or ironed down taking care to avoid trapping air between the sheet and the substrate.

Extruded or made-up tubes for pipe lining are coated with a tack solution and then slid into the pipe and inflated with air so that they loosely adhere to the wall of the pipe. The rubber tube is firmly applied to the pipe wall either by hand, using long handled rollers, or by drawing a suitable diameter plug through the pipe, thus expelling any air between the rubber tube and the pipe wall, and firmly attaching the rubber to the pipe.

Vulcanisation

Vulcanisation being a chemical reaction, is time/temperature dependant. In factory operations, vulcanisation is usually carried out in an autoclave using steam under pressure at temperatures up to 160°C. If the lined unit is a vessel too large to fit in an autoclave and has an adequate pressure rating, all outlets can be sealed and it can itself be pressurised. If this technique is employed then care must be taken, as a failure of the steam supply with consequent condensation, can cause a vacuum and subsequent collapse of the vessel.

Large, non-pressure vessels, which are usually lined on site in their final location, are normally vulcanised at 100°C using steam at ambient pressure or boiling water. Using such techniques, vulcanisation times will be extended and it is often necessary to shield the outside of the unit to minimise heat loss. Self vulcanising or chemical cure linings usually take up to eight weeks to fully vulcanise, but this process may be accelerated by injecting steam or hot air into the unit.

Polyurethane Linings

Polyurethane linings may be produced by spray-applied, build-up thickness methods, centrifugal casting for straight pipes, mould cast linings and pre-reacted sheet linings. High-quality reactive materials are usually produced in automatic mix dispensers which preheat, meter, mix and deliver the material to the required delivery point. As with rubber linings, the substrate is prepared by grit blasting followed by the application of a primer coat.

The polyurethane lining systems in use today are normally of the 100% solids type without solvents. The individual components, prepolymer and isocyanate are preheated and pumped to the mix/dispenser for metering and mixing. After mixing, the material is pumped through an orifice where it is

atomised and is then sprayed on the substrate. The substrate temperature rises due to the initial temperature of the applied polyurethane combined with reaction exotherm as the mixture cures. Modern polyurethane systems enable spraying to be continuous and so the required lining thickness is rapidly achieved.

Straight steel pipes up to 600 mm in diameter and six or more metres in length are usually lined by centrifugal casting. In this technique, the prepared preheated pipe is fitted with end caps and placed into the heated casting oven. Freshly mixed liquid polyurethane is then injected into the pipe which is then spun round its longitudinal axis until the polyurethane has cured to form a solid lining.

Pipe fittings such as bends, tees and crosses, unless large enough to enable spray application of the lining, are usually lined by casting using internal mould formers. The pipe fitting is assembled with the internal mould and preheated, the polyurethane mixture injected and the whole is oven cured.

Pre-reacted polyurethane sheet linings, usually made by cast moulding or centrifugal casting and slitting, are used for protecting surfaces against abrasion. They are not normally used for corrosive environment conditions as it is difficult to make a good joint seal between adjacent sheets to ensure a leak-free lining. They are usually tailored to fit the substrate geometry and attached with bolts which are subsequently protected by a polyurethane cap.

Inspection and Testing

It is essential that the lining is thoroughly tested prior to being put into service, as any faults could lead to substrate attack. Rectification of a failed unit is often very expensive, and there is also the risk of escape of corrosive contents which could lead to damage to the surrounding area. In the lining process, inspection and testing are carried out at each stage of the operation. All substrates are inspected prior to, and after, grit blasting to ensure they are suitable for lining.

The rubber lining is inspected before and after vulcanisation. A visual examination for mechanical damage, cuts, lack of adhesion, blisters and poor jointing is carried out over the entire lining surface. Continuity testing for pinholes is also carried out using either a high-frequency instrument based on a Tesla coil generating a high frequency discharge or a direct-current high-voltage instrument. Test voltages vary between 5 000 V and 50 000 V depending on the thickness and resistance of the lining being tested. The probe of the instrument is passed over the surface of the lining producing a corona discharge. The discharge concentrates at the point of any fault which is thus located.

Unless test coupons are produced alongside the lining, the only method of testing the vulcanisation state is with a hand hardness meter. A Shore 'A' or IRHD meter is used for soft rubber linings and a Shore 'D' meter for ebonites. The usual specification is that the hardness has to conform to $\pm 5^\circ$ of the specified hardness. There is no quantitative non-destructive test for the strength of the bond between the lining and the substrate and so such tests are usually carried out in the laboratory on a sample prepared from the materials used.

Elastomeric linings play an important role in industry where their resistance to highly corrosive environments allow many processes to be carried out in an economic manner. Major areas of use include heavy chemicals, dyestuffs, pharmaceuticals, electroplating, fertilisers, steel, foodstuffs, ore extraction, hydrometallurgical extraction of elemental metals and the water treatment industry.

Rubber lining is a specialist operation and should only be entrusted to competent, established companies who are continually developing lining material systems to keep ahead of the requirements of the process industries. Full consultation should always be held, prior to the final design stage, to ensure that the most-cost effective material specification is employed.

J. S. PITMAN

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